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(54) Title: **METHOD AND APPARATUS FOR GAS PURIFICATION**

(57) Abstract: This invention comprises an adsorption process for the removal of at least N₂O from a feed gas stream that also contains nitrogen and possibly CO₂ and water. In the process the feed stream is passed over adsorbents to remove impurities such as CO₂ and water, then over an additional adsorbent having a high N₂O/N₂ separation factor. In a preferred mode the invention is an air prepurification process for the removal of impurities from air prior to cryogenic separation of air. An apparatus for operating the process is also disclosed.

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METHOD AND APPARATUS FOR GAS PURIFICATION

[0001] This application claims the benefit of US provisional applications 60/342,673, filed December 20, 2001 and 60/384,611, filed May 31, 2002 the entire teachings of both are herein incorporated by reference.

FIELD OF THE INVENTION

[0002] This invention relates to the removal of N_2O , hydrocarbons, water vapor and CO_2 from gas streams, and more particularly to the removal of impurities from air, using adsorptive separation, prior to cryogenic separation of air.

BACKGROUND OF THE INVENTION

[0003] Cryogenic separation of air requires a pre-purification step to remove contaminants such as water, CO_2 and hydrocarbons from air. In cold sections of the separation process (such as heat exchangers and LOX sump), water and CO_2 can solidify and block the heat exchangers or other components in the distillation columns. Acetylene and other hydrocarbons in air present a potential hazard. The high boiling hydrocarbons can accumulate in the liquid oxygen and create an explosion hazard. Thus, those impurities in air must be removed in an adsorptive clean-up process prior to the cryogenic distillation of air.

[0004] Nitrous oxide (N_2O) should also be removed from air prior to separation. N_2O is currently present in air at a concentration of about 300-350 ppb, however, this concentration is increasing annually at a rate of about 0.3%. Various factors such as emissions from

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motor vehicles, HNO_3 plants, adipic acid and caprolactam plants (both use HNO_3 for oxidation of inorganics) contribute to this growing ambient concentration of N_2O . The presence of greater than 50 ppb of N_2O can be a serious problem for cryogenic air separation units (ASU) because it can form solid deposits in distillation columns. N_2O also decreases the solubility of CO_2 in liquid oxygen, thereby increasing the potential for freezing of CO_2 in the distillation columns. This can result in degraded performance and can even cause blockage of heat exchangers.

[0005] Air prepurification can be accomplished using pressure swing adsorption (PSA), temperature swing adsorption (TSA) or a combination of both (TSA/PSA) incorporating either a single adsorbent or multiple adsorbents. When more than one adsorbent is used, the adsorbents may be configured as discrete layers, as mixtures, composites or combinations of these. Impurities such as H_2O and CO_2 are commonly removed from air using two adsorbent layers in a combined TSA/PSA process. Normally, a first layer of activated alumina is used for water removal and a second layer of 13X molecular sieve is used for CO_2 removal. Prior art, such as U.S. 4711645, teaches the use of various adsorbents and methods for removal of CO_2 and water vapor from air.

[0006] Centi et al. (Ind. Eng. Chem. Res., vol. 39, pp 131-137, 2000) studied the behavior of various ion exchanged forms of ZSM5 Zeolites for removal of relatively high concentrations of N_2O (500ppm (parts per million) to 2000ppm) from industrial gas streams.

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ZSM5, being a high Si/Al ratio (2-200) zeolite, has less water affinity than its low Si/Al ratio counterparts. The best performance for N₂O removal in Centi's study is shown by Ba and Sr exchanged ZSM5. The paper indicates that in the presence of water, metal exchanged ZSM-5 has better N₂O adsorption properties than lower Si/Al ratio zeolites such as X and Y type zeolites.

[0007] U.S. 6,106,593 teaches a process, preferably TSA, that uses a three-layer adsorbent bed for successive removal of water, CO₂ and N₂O, wherein the preferred adsorbent is binderless CaX. Other adsorbents such as CaX (with binder), BaX and Na-mordenite are also recommended for the third layer. According to the patent, the criteria for selecting an adsorbent for N₂O removal is a Henry's law selectivity for N₂O compared to CO₂ of 0.49 or more at 30°C and a Henry's law constant for N₂O adsorption of at least 79 mmol/gm.

[0008] European patent application EP 0 862 938 teaches the placement of a zeolite adsorbent selected from X-zeolite, Y-zeolite, A-zeolite or mixtures thereof downstream of an alumina adsorbent in a PSA process to remove nitrogen oxides, such as NO, NO₂, N₂O and N₂O₃.

European Patent Application EP 0 995 477 teaches a method of removing at least a portion of N₂O in a gas stream using a type-X zeolite with a Si/Al ratio of 1.0-1.5 and containing a mixture of K⁺(<35%), Na⁺(1-99%) and Ca²⁺(1-99%) cations in various proportions.

[0009] European Patent Application (EP 1 092 465) teaches a TSA process (sequentially removing H₂O, CO₂ and N₂O and optionally hydrocarbons using a three-layer configuration of adsorbents. A NaLSX adsorbent is

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preferred in the second layer for CO₂ removal. A LSX zeolite (Si/Al=0.9-1.3), preferably CaLSX zeolite, is suggested for N₂O and hydrocarbon removal.

- [0010] European Patent Application EP 1 064 978 teaches the use of BaX zeolite to remove propane, ethylene and N₂O in a PSA or TSA process. The BaX zeolite contains at least 30% barium cations.
- [0011] U.S. 4,156,598 teaches the method of removing N₂O from nitrogen trifluoride by passing the gas through a synthetic zeolite adsorbent, such as sodium or calcium exchanged type X or type A zeolite.
- [0012] U.S. 4,933,158 teaches a method of removing N₂O and CO₂ from nitrogen trifluoride by passing the gas through a thermally treated zeolite selected from the group consisting of analcime, clinoptilolite, mordenite, ferrierite, phillipsite, chabazite, erionite and laumontite.
- [0013] U.S. 4,507,271 teaches the method of removing N₂O from a gas containing hydrogen, nitric oxide and nitrous oxide using A, X or Y zeolite.
- [0014] U.S. 5,587,003 discloses a method for removing substantially all of the CO₂ from air using the adsorbent clinoptilolite.
- [0015] Rege et al. (Chemical Engineering Science, vol. 55, pp 4827-4838, 2000) showed 13X adsorbent to provide better CO₂ removal from air than clinoptilolite. Rege also showed that Ca-exchanged clinoptilolite to have low N₂ adsorption.
- [0016] Catalytic decomposition of the contaminant is another means of removing an undesirable component from a gas mixture. A catalyst/adsorbent can be used much in the same way as described above except that the

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product of decomposition must be either removed as an additional contaminant or be an acceptable component of the gas mixture.

[0017] The prior art has typically derived its solution to the problem by seeking adsorbents with high N_2O to CO_2 selectivity. However, given the similar electronic structure of N_2O and CO_2 , and the nearly 1000-fold difference in gas phase concentration between N_2O and CO_2 in air, this methodology is difficult to apply. Thus an improved process and apparatus for the removal of N_2O and other impurities from air is required.

SUMMARY OF THE INVENTION

[0018] In a preferred embodiment of the invention, CO_2 and water are removed from the feed air, then an adsorbent having a high $\text{N}_2\text{O}/\text{N}_2$ separation factor is used for N_2O removal. Such adsorbent also has a higher Si/Al ratio and modest to low $\text{N}_2\text{O}/\text{CO}_2$ selectivity as compared to the prior art.

[0019] In a preferred embodiment, the invention relates to an adsorption process for the removal of N_2O from a gas containing N_2O , nitrogen and other components to produce a product gas, said process comprising passing said gas over a bed of one or more adsorbents, wherein at least one of the adsorbents is selected from the group consisting of clinoptilolite, chabazite and Li-exchanged zeolite or combinations thereof.

[0020] In a more preferred embodiment, the gas is air and the other components include water and CO_2 .

[0021] In one embodiment N_2O is in said gas in an amount of less than 100ppm.

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- [0022] In one embodiment the water and the CO₂ are adsorbed on an additional adsorbent prior to the gas passing over the clinoptilolite, chabazite or Li-exchanged zeolite.
- [0023] In one embodiment the process is an air prepurification process.
- [0024] In a preferred embodiment, at least 90% of the N₂O in the gas is adsorbed.
- [0025] In one embodiment the Li-exchanged zeolite is LiX.
- [0026] The invention also comprises a process for the separation of N₂O from a gas stream containing at least N₂O and nitrogen, said process comprising passing said gas stream over a bed of adsorbent having a working capacity ΔN₂O of greater than or equal to 3.56×10^{-4} at IBL.
- [0027] In a preferred embodiment the gas stream is air.
- [0028] In a preferred embodiment the adsorbent is selected from the group consisting of clinoptilolite, chabazite and Li-exchanged zeolite or combinations thereof.
- [0029] In a preferred embodiment the gas stream contains less than 100ppm N₂O.
- [0030] The invention also comprises an adsorption apparatus for the removal of N₂O from a gas containing N₂O, nitrogen and other components, said apparatus comprising one or more beds of at least a first adsorbent, wherein said first adsorbent is an N₂O selective adsorbent selected from the group consisting of clinoptilolite, chabazite and Li-exchanged zeolite.
- [0031] In a preferred embodiment the other components in the gas include H₂O and CO₂, and said apparatus further

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contains one or more additional adsorbents for the adsorption of H_2O and CO_2 , and wherein the additional adsorbents are upstream of said first adsorbent.

[0032] The process and apparatus of the present invention provide surprisingly superior N_2O removal efficiency over prior art processes and systems.

BRIEF DESCRIPTION OF THE DRAWINGS

[0033] Other objects, features and advantages will occur to those skilled in the art from the following description of preferred embodiments and the accompanying drawings, in which:

[0034] Fig. 1 is a schematic diagram of the breakthrough test apparatus;

[0035] Fig. 2 is a graph of N_2O breakthrough curves for NaX(2.5) for N_2O/N_2 and N_2O/He ;

[0036] Fig. 3 are nitrogen isotherms for certain adsorbents;

[0037] Fig. 4 are breakthrough curves to show initial breakthrough (0.05 ppm level);

[0038] Fig. 5 illustrates IBL N_2O loading for certain adsorbents (IBL:Initial breakthrough loading- N_2O adsorbed per unit weight of adsorbent at the 50 ppb breakthrough);

[0039] Fig. 6 is a schematic of an adsorption system useful for practicing the invention.

[0040] Fig. 7a illustrates a bed from a conventional prepurifier with an added layer for N_2O removal in accordance with the invention.

[0041] Fig. 7b illustrates a bed from a prepurifier with a first layer for water removal and a downstream mixed layer for CO_2 and N_2O removal.

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[0042] Fig. 7c illustrates a bed from a prepurifier with a first layer for water removal and a downstream mixed layer for hydrocarbon and N_2O removal.

[0043] Fig. 7d illustrates a bed from a prepurifier with a first layer for water removal a second layer for CO_2 removal, a third layer for removal of hydrocarbons and a final layer for N_2O removal.

DETAILED DESCRIPTION OF THE INVENTION

[0044] The invention is based upon first recognizing the critical components (N_2O/N_2) to be separated, then isolating these critical components in an adsorption zone within the adsorber and finally selecting an adsorbent that can efficiently affect the separation. The general problem to be solved is the removal of ppb levels (≈ 350 -400 ppb) of N_2O from a mixture of air containing other contaminants (including at least CO_2 and H_2O) prior to air separation by cryogenic means. In a process for removal of contaminants from a gas mixture by adsorption, it is common to adsorb contaminants successively in the order of decreasing adsorptivity and/or decreasing selectivity with respect to a chosen adsorbent. The effectiveness of such a process can often be improved by using a combination of adsorbents, configured in layers or mixtures, to enhance the removal of each contaminant, i.e. by selecting particular adsorbents to achieve maximum adsorptivity and or selectivity of each contaminant relative to the gas mixture. The use of different adsorbents disposed in layers in the adsorber is well known in the art.

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[0045] The selection of an adsorbent to remove a particular contaminant depends upon many factors, e.g. the type and composition of both the targeted contaminant and other gases in the mixture at the point of removal within the adsorber, the relative selectivity of the adsorbent for the contaminant(s) and non-contaminants, and the loading capacity of the adsorbent for the contaminant.

[0046] In a preferred embodiment of the invention, an adsorbent bed is first configured to remove substantially all of the CO_2 and H_2O from the feed stream (e.g. air) prior to removing N_2O . N_2O is then subsequently removed the partially purified feed stream. The present invention differs from the prior art in that an adsorbent is selected for the N_2O separation such that the adsorbent has both a high $\Delta\text{N}_2\text{O}/\Delta\text{N}_2$ separation factor and a high $\Delta\text{N}_2\text{O}$ (in the presence of high N_2 concentrations) capacity. Natural clinoptilolite, natural chabazite and LiX are preferred embodiments for N_2O removal from gases, particularly air, in accordance with the invention. With the addition of the N_2O adsorbent, the combination of all the adsorbents in the bed removes at least 90% and preferably all of the N_2O from the feed stream. Thus, the purified stream contains preferably less than 100 ppb (parts per billion), more preferably less than 50 ppb and most preferably less than 10ppb N_2O at the local stream conditions

[0047] Thus, this invention provides a simple and efficient way to substantially remove all of N_2O prior to cold box in cryogenic air separation plants, thereby

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ensuring a safe operation and potentially reducing liquid oxygen drainage.

[0048] The results of the present invention are even more surprising when evaluated in the context of the prior art selection criteria, i.e. the ratio of Henry Law constants for $\text{N}_2\text{O}/\text{CO}_2 > 0.49$ (U.S. 6,106,593). The ratio of Henry Law constants (ratio of initial isotherm slopes for $\text{N}_2\text{O}/\text{CO}_2$) was computed for clinoptilolite. This ratio was found to be about 0.40, well below the minimum recommended value of 6,106,593.

[0049] The prior art solution to the problem of removing N_2O from air has focused upon finding an adsorbent with high $\text{N}_2\text{O}/\text{CO}_2$ selectivity; however, this is difficult DUE to the similar electrostatic properties of these two adsorbates. Further electrostatic considerations do not recognize the significant effects of the relative concentrations of the adsorbates; e.g. in ambient air, CO_2 concentrations are typically 350 ppm to 400 ppm, one thousand times that of N_2O concentrations.

[0050] In the present invention because H_2O and CO_2 are almost completely removed prior to N_2O removal, the relevant separation is the removal of N_2O from N_2 . In this case, while electrostatics favor the selectivity of N_2O , the significant concentration difference (~790,000 ppm N_2 compared to ~350 ppb N_2O) favors the adsorption of N_2 . Thus in accordance with the present invention the adsorbent required has high $\text{N}_2\text{O}/\text{N}_2$ selectivity, low N_2 working capacity and sufficient N_2O working capacity to satisfy the purification requirements.

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[0051] In the practice of the present invention, adsorbent performance may be estimated by determining the working capacity of each of the primary adsorbates, i.e. N_2 and N_2O . The separation factor α , as defined below is utilized to evaluate the adsorbent effectiveness. This methodology is discussed in detail in US Patent 6,152,991.

$$\alpha = \frac{\Delta N_{2O}}{\Delta N_2} = \frac{w_{N_2O}(y,p,T)_{ads} - w_{N_2O}(y,p,T)_{des}}{w_{N_2}(y,p,T)_{ads} - w_{N_2}(y,p,T)_{des}} \quad (1)$$

where separation factor α is defined as the ratio of the working capacities. The numerator in this equation is the working capacity of N_2O , which is equal to the difference in loading w between adsorption and desorption conditions. The adsorption and desorption conditions are characterized by composition y , pressure p and temperature T .

[0052] In TSA air prepurification, maximum regeneration temperatures may vary from about 100°C to about 350°C. As a result, it is expected that the adsorbates (particularly atmospheric gases) will be completely thermally desorbed. Under such conditions, Equation (1) can be simplified as follows:

$$\alpha = \frac{\Delta N_{2O}}{\Delta N_2} = \frac{w_{N_2O}(y,p,T)_{ads}}{w_{N_2}(y,p,T)_{ads}} \quad (2)$$

[0053] When a contaminant is removed in a shallow adsorbent layer in TSA and significant resistance to

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mass transfer exists, the selectivity is redefined according to Equation (3):

$$\frac{\Delta X_A}{\Delta X_B} = \frac{\frac{m_{in}}{w_s} \int_0^{t_b} (y_{in} - y_{out}) dt}{X_B(y, P, T)_{ADS}} \quad (3)$$

The numerator in Equation (3) represents the working capacity of the adsorbent for the contaminant. m_{in} represents the molar feed flow into the bed, y_{in} and y_{out} are the inlet and outlet mole fractions of the minor component, respectively, w_s is the mass of adsorbent and t_b is the breakthrough time corresponding to a predetermined concentration. The denominator is the equilibrium capacity of the major component at the conditions at the end of the adsorption step, i.e. assuming complete desorption of all components. This situation may result when using small pore zeolites at conditions where the depth of the adsorbent layer is shorter than the mass transfer zone length.

[0054] This method is superior to prior art methods for evaluating the selectivity of N_2O in that the working capacities are determined at the partial pressure of each individual component at the relevant process conditions. Furthermore, coadsorption effects are incorporated in the determination of the loadings. The analysis can be performed using either a multicomponent isotherm model supported by pure component data (e.g. loading ratio correlation isotherm model) or directly from experimental data. Since the concentration of N_2 is overwhelming compared to N_2O , the coadsorption effect of N_2O upon N_2 is negligible. Thus, the denominator of Equation (2) or Equation (3) may be

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obtained directly from the measured pure-component N_2 isotherm.

[0055] Conversely, the coadsorption of N_2 has a very significant effect upon the adsorption of N_2O . If accurate low concentration pure-component isotherm data for N_2O is available or attainable, then Equation (2) may be applied to assess working capacity and selectivity. Otherwise, it is preferred to determine the working capacity for N_2O directly under coadsorption conditions with N_2 using the breakthrough test method, which is well known to those skilled in the art. This allows any kinetic effects to be incorporated into the working capacity as well. The breakthrough tests allow for the determination of the equilibrium capacity of a component at saturation, and the breakthrough capacity and time at some defined breakthrough level, e.g. 50 ppb.

[0056] In order to evaluate adsorbents for N_2O working capacity and separation factor according to Equation (3), a breakthrough test apparatus was constructed as shown in Figure 1.

[0057] The adsorbents tested were obtained from the sources listed below. The natural adsorbents (clinoptilolite and chabazite) were obtained from Steelhead Specialty Minerals, WA. Synthetic zeolites were obtained from various manufacturers: Zeolyst (ZSM5, mordenite), Zeochem (CaX(2.5) and >85% Ca) and UOP (13X, NaX(2.3), LiX(2.3) >97% Li; LiX(2.0) >97% Li, NaY). Note that the numbers recited in the parentheses (e.g. 2.5, 2.3, and 2.0) refer to SiO_2/Al_2O_3 ratio. All of the adsorbents were thermally regenerated at 350°C, 1.0 bar pressure and under N_2 purge for approximately

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16 hours before each test. After regeneration the adsorbents were allowed to cool to the test temperature of 27°C.

[0058] Breakthrough tests were conducted using the following feed gas mixtures: 1.0 ppm N₂O in N₂ and 1.0 ppm N₂O in He. Also, N₂ isotherms were determined gravimetrically. The results from these tests were examined to determine N₂O separation factor and working capacity. Tests were performed to saturation, i.e. until the effluent N₂O concentration reached the feed level concentration. For evaluating various adsorbents, a N₂O concentration of 1.0 ppm was selected. All of the breakthrough tests were performed at 6 bar, 300 K and an inlet gas flowrate of approximately 21.3 slpm (0.08 kmol/m² s) using an adsorption column length of either 22.9 cm or 5.6 cm. The feed conditions are representative of conditions at the inlet of an air prepurifier for a typical cryogenic air separation plant. Breakthrough curves were also generated using 1.0 ppm N₂O in He and 1.0 ppm CO₂ in He to determine pure-component N₂O or CO₂ loadings, respectively. In order to determine the coadsorption effects of N₂O and CO₂ in N₂, breakthrough tests were also performed using 1.0 ppm N₂O + 1.0 ppm CO₂ in N₂. Initial breakthrough was established at 50.0 ppb N₂O and initial breakthrough loading (IBL) was determined as the average amount of N₂O adsorbed per unit weight of adsorbent at the 50.0 ppb breakthrough.

[0059] Breakthrough tests are conducted in the following manner using the apparatus shown in Figure 1. A challenge gas from source 1 containing the contaminant(s) of interest (e.g. 10 ppm N₂O in N₂) is

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metered through flow controller 3, and mixes in a gas mixer 5 with high purity diluent N_2 or He from source 2 and provided at a prescribed flowrate through a flow controller 4 to achieve the desired feed concentration of contaminant(s). This mixed challenge gas is then fed to the test bed 6 containing the adsorbent. The effluent is passed through a flow meter 7 to the N_2O analyzer 8 (TEI Model 46-C) where the breakthrough concentration of N_2O is monitored as a function of time. Control valve 9 is used to maintain the desired pressure in the system. The piping and adsorbent bed are maintained at the same temperature as the feed by immersing them in a thermostat bath (not shown).

The following are non-limiting examples that illustrate the methodology for selecting adsorbents and their implementation in accordance with the invention.

Example 1. N_2 Coadsorption Effects

[0060] Adsorbents were tested as described above to determine the effect of N_2 coadsorption upon the adsorption of N_2O . The results of the saturation capacity of N_2O (1.0 ppm) in N_2 and in He on various adsorbents are compared in Table 1 below. These results were determined for feed conditions of 6.0 bar, 300°K and 0.08 kmol/m² s molar flux using a 22.9 cm or 5.6 cm adsorbent bed length. The SiO_2/Al_2O_3 ratio is specified for some adsorbents in the table, e.g. NaX ($SiO_2/Al_2O_3 = 2.3$). Figure 2 shows N_2O breakthrough curves for adsorbent 13X (NaX 2.5) for N_2O in N_2 and N_2O in He.

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[0061] Table 1: Effect of N₂ Coadsorption Upon N₂O Loading

Material	N ₂ O loading (mmol/gm) 1.0 ppm N ₂ O/He	N ₂ O loading (mmol/gm) 1.0 ppm N ₂ O/ N ₂	Preferred Adsorbents
NaY	4.06×10^{-4}	1.42×10^{-4}	
NaZSM5	1.7×10^{-3}	3.59×10^{-4}	
NaKX		4.58×10^{-4}	
13X NaX (2.5)	9.55×10^{-4}	6.09×10^{-4}	
NaX (2.3)	1.73×10^{-3}	7.03×10^{-4}	
CaX		1.98×10^{-3}	
Na-Mordenite		6.38×10^{-3}	
Clinoptilolite (CS400)	8.86×10^{-2}	3.60×10^{-3}	X
LiX (2.3)	5.5×10^{-3}	1.22×10^{-3}	X
LiX (2.0)	6.7×10^{-3}	1.74×10^{-3}	X
Chabazite	6.75×10^{-2}	3.42×10^{-3}	X
Clinoptilolite (TSM140)	6.84×10^{-2}	8.20×10^{-3}	X

[0062] These results clearly show the substantial effect of N₂ coadsorption, resulting in a decrease in N₂O capacity from 36% to 96% compared to the single component saturation capacity (1.0 ppm N₂O in He). The fourth column of Table 1 also indicates examples of preferred adsorbents of the invention (i.e. adsorbents with high N₂O loading in the presence of N₂).

Example 2. N₂ Isotherms

[0063] Isotherms for N₂ at 300°K were determined for various adsorbents over a range of pressures which included typical feed pressures to a prepurifier of a cryogenic air separation unit. Example isotherms are shown in Figure 3. The pure component N₂ loadings from

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these isotherms are compared in Table 3 for various adsorbents at 6.0 bar.

Table 2. Equilibrium Loadings of
N₂ at 6.0 bar, 300°K

Material	N ₂ loading (mmol/gm)
Silicalite	0.68
H-ZSM5	0.74
4A	1.11
NaY	0.85
NaZSM5	
NaKX	0.86
13X NaX (2.5)	1.30
NaX (2.3)	1.33
CaX	1.53
Na-Mordenite	1.40
Clinoptilolite (CS400)	0.64
LiX (2.3)	1.71
LiX (2.0)	2.29
Chabazite	1.22
Clinoptilolite (TSM140)	1.23

Example 3. Breakthrough at 50 ppb N₂O

[0064] The average N₂O loading (IBL) of the adsorbent bed was determined at 50.0 ppb N₂O from the same N₂O/N₂ tests reported in Table 1 above. Typical breakthrough results are illustrated in Figure 4. The IBL values (reflecting not only the 50 ppb breakthrough, but also N₂ coadsorption) are compared for various adsorbents in Table 3 and shown in Figure 5. Separation factors were also computed using Equation 3. The N₂ loadings at 6 bar from Table 2 are used in Equation 3 to represent the working capacity of N₂ in the process.

[0065] N₂O working capacities can be computed either from the saturation loadings of N₂O/N₂ or from the average

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loadings of N_2O at the IBL. The separation factor computed from the average loadings at the IBL is the preferred method since it reflects both the equilibrium and dynamic effects of the adsorbent. Nevertheless, the former method (which reflects equilibrium effects only) is acceptable when only isotherms and no breakthrough data are available. Both separation factors are tabulated in Table 3 for various adsorbents. Both methods identify clinoptilolite (TSM-140) as having the highest N_2O/N_2 separation factor, as well as establishing the same group of six adsorbents with higher separation factors compared to the prior art choice of CaX. The order of effectiveness amongst the adsorbents in the preferred group is affected by which separation factor method is used.

[0066] Using the methodology of the invention, clinoptilolite TSM-140 is the most preferred adsorbent for removing N_2O from air. This adsorbent has the highest N_2O working capacity at IBL, the highest working N_2O/N_2 separation factor and a moderate N_2 working capacity. It is evident from Table 3 that TSM140 has approximately 6.6 times the average N_2O breakthrough capacity of CaX. Thus, clinoptilolite TSM140 provides a surprisingly superior solution to the problem.

Table 3: IBL and α for Various Adsorbents

Material	IBL (mmol/gm)	α (Eqn 3) N ₂ O @ IBL	α (Eqn 3) N ₂ O @ 1.0ppm
Silicalite	2.20×10^{-5}	3.24×10^{-5}	1.11×10^{-4}
Activated carbon	2.60×10^{-5}		
H-ZSM5	3.60×10^{-5}	4.89×10^{-5}	1.85×10^{-4}
4A	4.30×10^{-5}	3.87×10^{-5}	
NaX	5.20×10^{-5}	6.09×10^{-5}	1.67×10^{-4}
NaZSM5	6.50×10^{-5}		
NaKX	1.32×10^{-4}	1.54×10^{-4}	5.33×10^{-4}
13X NaX (2.5)	1.87×10^{-4}	1.44×10^{-4}	4.68×10^{-4}
NaX (2.3)	2.27×10^{-4}	1.71×10^{-4}	5.29×10^{-4}
CaX	2.40×10^{-4}	1.57×10^{-4}	1.29×10^{-3}
Na-Mordenite	3.13×10^{-4}	2.24×10^{-4}	4.56×10^{-3}
Clinoptilolite (CS400)	3.56×10^{-4}	5.57×10^{-4}	5.64×10^{-3}
LiX (2.3)	3.82×10^{-4}	2.23×10^{-4}	7.10×10^{-4}
LiX (2.0)	7.68×10^{-4}	3.35×10^{-4}	7.61×10^{-4}
Chabazite	1.04×10^{-3}	8.55×10^{-4}	2.81×10^{-3}
Clinoptilolite (TSM140)	1.58×10^{-3}	1.28×10^{-3}	6.64×10^{-3}

Example 4: N₂O and CO₂ Coadsorption Effects

[0067] In the present invention, the adsorber is preferably configured so that the water vapor and CO₂ contaminants in the feed air are substantially removed from the gas mixture prior to the final clean up of the stream in which N₂O is adsorbed. Sufficient removal of N₂O must be affected to prevent breakthrough beyond 50 ppb N₂O during the adsorption step of the prepurifier cycle. In this situation, it is estimated that low levels of CO₂ (less than 10.0 ppm, most likely less than 1.0 ppm) could be present with 100 ppb or more N₂O with the remaining bulk gas being of air composition (N₂/O₂). In order to verify the effectiveness of the adsorbent and to determine the competitive coadsorption effects of CO₂ upon N₂O, breakthrough tests were performed with clinoptilolite TSM140 using a feed

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mixture with 1.0 ppm CO₂ and 1.0 ppm N₂O in N₂. The results are shown in Table 4 for the average IBL loading and saturated loadings of N₂O. The loadings are comparable within the experimental error with the N₂O loadings from Tables 1 and 3. Thus, it is evident that CO₂ and N₂O do not compete with each other at these low concentrations, i.e. each competes individually only with N₂. This can be explained by the fact that the number of adsorbed molecules of N₂ (Table 3) is far greater than either those adsorbed molecules of N₂O or CO₂. As N₂O or CO₂ enter the adsorbent the adsorption sites are predominantly occupied by N₂ molecules.

Table 4: IBL and saturation loadings (1 ppm N₂O+1 ppm CO₂ in N₂)

IBL N ₂ O (mmol/gm)	N ₂ O saturation loading (mmol/gm)
1.6×10^{-3}	8.3×10^{-3}

[0068] These results suggest that other low-level contaminants present in the gas stream can also be removed simultaneously with N₂O. In the case of clinoptilolite, adsorbates with a kinetic diameter less than about 4.5Å and with an interaction potential energy greater than that of N₂ are likely to completely or partially removed. Such adsorbates include but are not limited to acetylene, ethylene and propane.

Example 5: Prepurifier operation

[0069] A two-bed TSA prepurifier was designed to evaluate the adsorbent requirement for complete N₂O removal.

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The inlet air flow was 569,000 NCFH at a pressure of 72 psig, and an ambient temperature of about 78 F. The ambient N₂O level was about 400 ppb and the CO₂ level was about 400 ppm. Average temperature of air going into the prepurifier was about 44.6 F. Each bed has an internal diameter of 8.0 ft.

[0070] Initially the bed has two layers: First layer of Alumina (9.9 in) and the second layer of 13X APG (46.5 in). The breakthrough level of N₂O was monitored for this two-layered bed system. It was found that about 80% of the entering N₂O in each cycle is retained in the bed. About 20% of the incoming N₂O breaks through the bed. The thickness of the clinoptilolite TSM 140 layer needed to ensure complete N₂O removal if this layer is added downstream of 13 X layer was calculated to be about 9 in. Therefore, a very thin layer of clinoptilolite TSM140 added downstream of 13X layer substantially eliminates the problem of N₂O leaking into the cold box. The resulting prepurifier with the three layers could substantially eliminate all of water vapor, CO₂ and N₂O and most of the hydrocarbons entering the bed.

[0071] The Si/Al ratio and the composition (% of exchangeable cations) of major cations in clinoptilolite TSM140 and CS400 are given in Table 5. It is evident from the working capacity in Table 1 and the selectivity in Table 3 that TSM140 has superior ability to remove N₂O in the presence of high concentrations of N₂ compared to CS400. Although both materials are of clinoptilolite structure with nearly the same Si/Al ratio, the efficiency of adsorption of N₂O is quite different. A primary difference in the

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composition of these materials is in the amount of Na cation present. We have found that a preferred clinoptilolite would have sodium in an amount between about 30 to about 80% of the exchangeable cations.

Table 5: Composition of natural adsorbents

	TSM140	CS400
Si/Al	4.84	4.78
% Ca	12	34
% Na	62	14
% K	19	32
% Mg	7	20

[0072] As indicated above, clinoptilolite (most preferably TSM140 and CS400), chabazite and LiX (most preferably having a greater than 86% Li exchange and a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of (2.3) or (2.0)) were found to be the preferred adsorbents for removing N_2O from air prior to cryogenic air separation.

[0073] The natural zeolites clinoptilolite and chabazite, having higher Si/Al ratio (3.0 to 5.0 in this invention) than type X zeolites, are "weaker" adsorbents compared to LiX, CaX and NaX. These natural zeolites also have a smaller micropore volume than type X. These factors contribute to the lower N_2 adsorption capacity and selectivity; however, overall capacity is typically not a critical issue when removing trace quantities of contaminants. Conversely, because of the higher Si/Al ratio of clinoptilolite and chabazite, these materials have fewer cations. This generally means weaker energetics in relation to polar adsorbates. While this favors weaker attraction for N_2 it also means weaker attraction for N_2O as well.

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[0074] The adsorption characteristics of zeolites are strongly dependent upon their cation composition. Both the equilibrium and kinetic adsorption properties can be altered by ion exchange. Cation type, location and number can completely alter adsorption behavior. Acid washing of small pore natural zeolites may remove impurities that block the pores, progressively eliminate cations and finally dealuminate the structure as the strength and duration of the treatment increases. Alkali washing has been shown to modify both the pore size and pore volume of clinoptilolite. The method and extent of dehydration is important in determining the adsorption properties and structural stability of activated zeolites. Dehydration and thermal treatment can result in cation migration, thereby influencing cation location and pore openings. Any of the methods may be used to further improve the adsorption characteristics of the preferred adsorbents of this invention, i.e. equilibrium and/or kinetic adsorption properties may be effected.

[0075] As indicated previously, the invention relates to the removal of N_2O from air in which the H_2O and CO_2 have already been substantially removed. By "substantially removed" we mean removed to levels of less than 10ppm, preferably less than 1.0 ppm. However, the invention may be applied in removing N_2O in the presence of higher concentrations of CO_2 and/or H_2O . In the most direct application of the invention, a layer of the N_2O -selective adsorbent is located downstream (as determined by the direction of feed flow during adsorption) of those adsorbents that are used to remove H_2O and CO_2 . Typical TSA prepurifiers have

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either a single layer of zeolite to remove both H₂O and CO₂ or a layer of activated alumina (for H₂O removal) followed by a layer of zeolite for CO₂ adsorption. In general, adsorbents useful for the water and CO₂ adsorption are known to those skilled in the art and include cation containing zeolites (synthetic or natural), activated alumina, silica gel and activated carbon.

[0076] In such configurations, the N₂O-selective layer would represent either a second or third layer of adsorbent, respectively, in the prepurifier adsorber. Other alternative configurations contemplated by this invention are described below. According to the invention N₂O is adsorbed onto at least one adsorbent selected from natural clinoptilolite, natural chabazite and Li exchanged X zeolite. The removal of N₂O from the gas stream is achieved by passing the gas stream through a bed of clinoptilolite, chabazite or LiX or a mixture of these in the temperature range of about -70°C to 80°C, preferably 0°C to 40°C. While the invention is directed at the removal of low concentrations of N₂O from air, it may also be used to remove higher concentrations of N₂O from air or other gas mixtures. Typical gases that can be purified by this process include air, nitrogen, oxygen, argon, methane etc.

[0077] The process of N₂O removal is carried out preferably in a cyclic process such as pressure swing adsorption (PSA), temperature swing adsorption (TSA), vacuum swing adsorption (VSA) or a combination of these. Such processes can be used for removing ppm or ppb levels of N₂O present in air prior to cryogenic

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separation. The process of the invention may be carried out in single or multiple adsorption vessels operating in a cyclic process that includes at least the steps of adsorption and regeneration. The adsorption step is carried out at pressure range of 1.0 to 25 bar and preferentially from about 3 to 15 bar. The temperature range during the adsorption step is -70°C to 80°C. When a PSA process is used, the pressure during the regeneration step is lower than the adsorption pressure, preferably in the range of about 0.20 to 10.0 bar, and preferably 1.0 to 2.0 bar. For a TSA process, regeneration is carried out at a temperature greater than the adsorption temperature; preferably in the range of about 50°C to 400°C, more preferably between 100°C to 300°C. In cryogenic air separation processes, the regeneration gas is typically taken from the product or waste N₂ or O₂ streams.

[0078] In the cyclic process, the gas containing N₂O is introduced at one end of an adsorption vessel that contains at least a layer of N₂O-selective adsorbent. As the gas passes through the bed, N₂O is adsorbed and an essentially N₂O-free gas is obtained at the other end of the bed. As the adsorption step proceeds, a N₂O front develops in the bed and moves forward through the bed during the adsorption step. When the front reaches the end of the bed, which is determined by the concentration of N₂O acceptable in the outlet gas, the adsorption step is terminated and the vessel enters the regeneration mode. The method of regeneration depends upon the type of cyclic process. For a PSA process, generally the vessel is countercurrently depressurized. Subatmospheric pressure levels can be additionally

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employed during the regeneration steps using a vacuum pump. For a TSA process, regeneration of the adsorbent bed is achieved by passing heated gas countercurrently through the bed. Using the thermal pulse method, a cooling purge step follows the hot purge step. The heated regeneration gas may also be provided at a reduced pressure (relative to the feed) so that a combined TSA/PSA process is affected. For removal of N_2O from air, the TSA/PSA method is preferred.

[0079] In some cases, passing an inert or weakly adsorbed purge gas countercurrently through the bed can further clean the adsorbent bed. In a PSA process, the purge step usually follows the countercurrent depressurization step. In a TSA process, the heated purge gas can be used for regeneration of adsorbent. In case of a single vessel system, the purge gas can be introduced from a storage vessel, while for multiple bed system, purge gas can be obtained from another adsorber that is in the adsorption phase.

[0080] The adsorption system can have more steps than the two basic fundamental steps of adsorption and desorption. For example, top to top equalization or bottom to bottom equalization can be used to conserve energy and increase recovery.

[0081] In a specific embodiment, the prepurification process operates as follows with reference to Fig. 6. Referring to Figure 6, feed air fed to the system via conduit 23 is compressed in compressor 10 and cooled by chilling means 11 prior to entering one of two adsorbers (16 and 17) where at least the contaminants H_2O , CO_2 and N_2O are removed from the air. The purified air exits the adsorber via conduit 24 and then enters

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the air separation unit (ASU) (not shown) where it is then cryogenically separated into its major components N_2 and O_2 . In special designs of the ASU, Ar, Kr and Xe may also be separated and recovered from the air. While one of the beds is adsorbing the contaminants from air, the other is being regenerated using purge gas provided via conduit 25. A dry, contaminant-free purge gas may be supplied from the product or waste stream from the ASU or from an independent source to desorb the adsorbed contaminants and thereby regenerate the adsorber and prepare it for the next adsorption step in the cycle. The purge gas may be N_2 , O_2 , a mixture of N_2 and O_2 , air or any dry inert gas. In the case of thermal swing adsorption (TSA), the purge gas is first heated in heater 22 prior to being passed through the adsorber in a direction countercurrent to that of the feed flow in the adsorption step. TSA cycles may also include a pressure swing. When only pressure swing adsorption (PSA) is utilized, there is no heater.

[0082] The operation of a typical PSA cycle is now described in reference to Figure 6 for one adsorber. One skilled in the art will appreciate that the other adsorber vessel will operate with the same cycle, only out of phase with the first adsorber in such a manner that purified air is continuously available to the ASU. Feed air is introduced via conduit 23 to compressor 10 where it is pressurized. The heat of compression is removed in chilling means 11, e.g. a mechanical chiller or a combination of direct contact after-cooler and evaporative cooler. The pressurized, cool and H_2O -saturated feed stream then enters adsorber 16. Valve

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12 is open and valves 14, 18 and 20 are closed as the adsorber vessel 16 is pressurized. Once the adsorption pressure is reached, valve 18 opens and purified product is directed to the ASU with conduit 25 for cyrogenic air separation. When the adsorber 16 has completed the adsorption step, valves 18 and 12 are closed and valve 14 is opened to blow down the adsorber 16 to a lower pressure, typically near ambient pressure. Once depressurized, valve 20 is opened and heated purge gas is introduced into the product end of the adsorber 16. At some time during the purge cycle, the heater is turned off so that the purge gas cools the adsorber to near the feed temperature.

[0083] One of ordinary skill in the art will further appreciate that the above description represents only an example of a typical prepurifier cycle, and there are many variations of such a typical cycle that may be used with the present invention. For example, PSA may be used alone wherein both the heater 22 and the chilling means 11 may be removed. Pressurization may be accomplished with product gas, feed gas or a combination of the two. As indicated above, bed-to-bed equalization may also be used and a blend step may be incorporated where a freshly regenerated bed is brought on line in the adsorption step with another adsorber nearing completion of its adsorption step. Such a blend step serves to smooth out pressure disturbances due to bed switching and also to minimize any thermal disturbances caused when the regenerated bed is not completely cooled to the feed temperature. Furthermore, the invention may be practiced with a prepurifier cycle not limited to two adsorber beds.

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[0084] As indicated above, the most preferred embodiment of the present invention is the removal of trace amounts of N_2O from gaseous streams, particularly from air prior to cryogenic separation. The method of the invention is particularly applicable to the removal of low to intermediate (e.g. ppb to ppm) concentrations of N_2O from a feed stream. For example, the methodology is particularly useful in air prepurification (prior to cryogenic distillation) where the N_2O concentration is on the order of 350ppb. The adsorbents are also especially effective for the removal of N_2O from gas streams containing 100ppm or less N_2O . If the gas contains water vapor, this should most preferably be removed to a level of less than 100 ppb prior to passing it through the N_2O adsorbent. If the gas contains CO_2 , CO_2 should be removed to levels less than 10 ppm, preferably less than 1ppm, however, removal of CO_2 is not as essential as removal of water vapor. The relative thickness of the N_2O layer depends upon the pressure, temperature, composition and flow of the feed gas and the desired purity of the purified gas, but could be determined by one of ordinary skill in the art.

[0085] As indicated above, in a preferred air prepurification embodiment of the invention, water vapor and CO_2 are substantially removed from air on at least one layer of activated alumina or zeolite, or by multiple layers of activated alumina and zeolite prior to passing the air stream through the N_2O adsorbent layer. Optionally, the N_2O -selective adsorbent layer may be extended and used to remove part or all of the CO_2 from air. Alternately, in an adsorption vessel, a

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first layer of alumina can be used to remove water vapor and a next layer comprised of a mixture of the N_2O -selective adsorbent and 13X (or other zeolite) can be used to remove both CO_2 and N_2O from the air. Such an adsorbent mixture may be composed of physically separate adsorbents or of different adsorbents bound together in the form of a composite. Additionally, the N_2O selective adsorbent may be deposited in the form of fine particles on a substrate such as a monolith.

[0086] In the existing prepurifier beds with water adsorbent layer and CO_2 adsorbent layer, the method of the invention allows for replacing 10-100% of CO_2 adsorbent layer with the N_2O adsorbent at the most downstream end.

[0087] As illustrated in Figs. 7a and 7b various layered arrangements of a bed 30 are possible. Figure 7a shows for example a bed 30 arrangement comprising a layer of a first adsorbent for water removal 31; a layer 32 of a second adsorbent for CO_2 removal; and a third layer 33 that is the N_2O adsorbent.

[0088] In Figure 7b, a bed 30 arrangement having a first layer of water adsorbent 31', and a second layer 34 that is a mixture or composite of a CO_2 adsorbent and the N_2O adsorbent

[0089] Some chemically modified forms of the adsorbents used in the process of this invention would also be appropriate for N_2O removal purposes. Thus, the method of the invention can be carried out wherein said clinoptilolite and chabazite are natural or synthetic, and have exchangeable cations from ions of Group 1A, Group 2A, Group 3A, Group 3B, the lanthanide series of the Periodic Table, as well as mixtures of these.

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According to the invention, at least nitrous oxide gas contained in a gas stream is separated, whereby N_2O is adsorbed on at least one adsorbent or a mixture of these selected from the following: natural clinoptilolite, natural chabazite and Li exchanged X zeolite. The mixture can be made with any ratio of these adsorbents namely 0-100% clinoptilolite, 0-100% chabazite and 0-100% LiX, wherein the total of these is 100%.

[0090] The adsorbent beds used in the method of the invention can have variety of configurations such as vertical beds, horizontal beds or radial beds and can be operated in a pressure swing adsorption mode, temperature swing adsorption mode, vacuum swing adsorption mode or a combination of these.

[0091] Clinoptilolite has excellent thermal stability at very high temperatures up to $700^{\circ}C$. Thus, it can be regenerated at very high temperatures if needed.

[0092] Since clinoptilolite and chabazite are natural zeolites mined from the earth, they should be thermally treated before being used in the method of the invention. These natural zeolites should also be ground to a suitable average grain size, for example, 4 to 50 mesh, preferably 8 to 12 mesh (US Sieve Series), although smaller or larger average sizes may be employed depending upon the requirements of the application.

[0093] In the method of the invention, the ground natural mineral with predetermined grain size distribution is thermally treated at a temperature of $250^{\circ}C$ to $700^{\circ}C$. It is important to dehydrate the zeolites to less than 1.0 % (wt) H_2O . Those skilled in

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the art are familiar with such sizing and calcination procedures.

[0094] The adsorbents in this method may be shaped by a series of methods into various geometrical forms such as beads and extrudates. This might involve addition of a binder to zeolite powder in ways very well known to prior art. These binders might also be necessary for tailoring the strength of the adsorbents. Binder types and shaping procedures are well known to prior art and the current invention does not put any constraints on the type and percentage amount of binders in the adsorbents.

[0095] The N_2O adsorbent could also potentially adsorb some hydrocarbons from air. To ensure complete removal of hydrocarbons, the N_2O adsorbent can be physically mixed in a layer 35 with a hydrocarbon selective adsorbent such as 5A (Bed 30 in Figure 7c). Alternately, an additional layer of hydrocarbon selective adsorbent can be placed upstream (layer 36) or downstream (not shown) of the N_2O adsorbent layer 33'' (Bed 30 in Figure 7d). Note that 31'' and 31''' refer to a layer of water adsorbent and 32' and 32'' refer to a layer of CO_2 adsorbent in Figures 7c and 7d respectively.

[0096] The term "comprising" is used herein as meaning "including but not limited to", that is, as specifying the presence of stated features, integers, steps or components as referred to in the claims, but not precluding the presence or addition of one or more other features, integers, steps, components, or groups thereof.

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[0097] Specific features of the invention are shown in one or more of the drawings for convenience only, as each feature may be combined with other features in accordance with the invention. Alternative embodiments will be recognized by those skilled in the art and are intended to be included within the scope of the claims.

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What is claimed is:

- [0001] 1. An adsorption process for the removal of N_2O from a gas containing N_2O , nitrogen and other components, said process comprising passing said gas over a bed of one or more adsorbents and producing a purified gas, wherein said one or more adsorbents is selected from the group consisting of clinoptilolite, chabazite and Li-exchanged zeolite.
- [0002] 2. The process of claim 1, wherein said gas is air.
- [0003] 3. The process of claim 1, wherein said other components include water and CO_2 .
- [0004] 4. The process of claim 1, wherein said N_2O is in said gas in an amount of less than 100ppm.
- [0005] 5. The process of claim 3, wherein said water and said CO_2 are adsorbed on an additional adsorbent prior to said gas passing over said clinoptilolite, chabazite or said Li-exchanged zeolite.
- [0006] 6. The process of claim 1, wherein said gas is air.
- [0007] 7. The process of claim 1, wherein said process is either pressure swing adsorption or temperature swing adsorption.

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- [0008] 8. The process of claim 1, wherein said process is a combination of temperature swing adsorption and pressure swing adsorption.
- [0009] 9. The process of claim 5, wherein at least 90% of the N_2O in said gas is adsorbed.
- [0010] 10. The process of claim 1, wherein said adsorbent is clinoptilolite, and wherein between 30% and 80% of its exchangeable cations are sodium cations.
- [0011] 11. The process of claim 1, wherein said adsorbent has been washed with an acid or alkali solution prior to being placed in said bed.
- [0012] 12. The process of claim 1, wherein said Li-exchanged zeolite is LiX.
- [0013] 13. The process of claim 1, wherein said product gas contains less than 100ppb of N_2O .
- [0014] 14. The process of claim 1, wherein said product gas contains less than 50ppb of N_2O .
- [0015] 15. The process of claim 1, wherein said product gas contains less than 10ppm of N_2O .
- [0016] 16. The process of claim 8, wherein in said pressure swing adsorption process, adsorption takes place at a pressure between 1.0 to 25 bar, and desorption takes place at a pressure between 0.2 to 10.0 bar.

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- [0017] 17. The process of claim 8, wherein in said temperature swing adsorption process, adsorption takes place at a temperature between -70 degrees Celsius and 80 degrees Celsius, and desorption takes place at a greater temperature than said adsorption.
- [0018] 18. A process for the separation of N₂O from a gas stream containing at least N₂O and nitrogen, said process comprising passing said gas stream over a bed of adsorbent having a ΔN_2O working capacity of greater than or equal to 3.56×10^{-4} at IBL.
- [0019] 19. The process of claim 18, wherein said gas stream is air.
- [0020] 20. The process of claim 18, wherein said adsorbent is selected from the group consisting of clinoptilolite, chabazite and Li-exchanged zeoliteor combinations thereof.
- [0021] 21. The process of claim 18, wherein said gas stream contains less than 100ppm N₂O.
- [0022] 22. The process of claim 18, wherein the $\Delta N_2O/\Delta N_2$ selectivity is greater than or equal to 2.23×10^{-4} at IBL.
- [0023] 23. An adsorption apparatus for the removal of N₂O from a gas containing N₂O, nitrogen and other components, said apparatus comprising one (30) or more

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beds of at least a first adsorbent, wherein said first adsorbent is an N_2O selective adsorbent selected from the group consisting of clinoptilolite, chabazite and Li-exchanged zeolite or combinations thereof.

[0024] 24. The apparatus of claim 23, wherein said other components include H_2O and CO_2 , and said apparatus further contains one or more additional adsorbents for the adsorption of H_2O and CO_2 , and wherein said additional adsorbents are upstream of said first adsorbent.

[0025] 25. The apparatus of claim 24, wherein said additional adsorbents are one or more of cation exchanged natural zeolites, cation exchanged synthetic zeolites, alumina, silica gel and activated carbon.

[0026] 26. The apparatus of claim 24, wherein said N_2O selective adsorbent is in a separate layer from said additional adsorbents.

[0027] 27. The apparatus of claim 23, wherein said apparatus comprises a layer of alumina and a mixed layer of said N_2O selective adsorbent and an adsorbent selective for CO_2 downstream of said layer of alumina.

[0028] 28. The apparatus of claim 23, wherein said apparatus comprises a layer of alumina and, downstream therefrom, a layer of a composite material comprising said N_2O selective adsorbent and an adsorbent selective for CO_2 bound into a single particulate material.

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- [0029] 29. The apparatus of claim 23, wherein said additional adsorbents are in separate layers.
- [0030] 30. The apparatus of claim 23, wherein said adsorbent is in the form of particles having an average size that is selected between 4-50 mesh.
- [0031] 31. The apparatus of claim 23, wherein said apparatus contains two beds (16, 17).
- [0032] 32. The apparatus of claim 1, wherein said one or more beds contain a second additional adsorbent for the removal of hydrocarbons.
- [0033] 33. The apparatus of claim 32, wherein said second additional adsorbent is either in its own layer, or is mixed with said first adsorbent(s).
- [0034] 34. The apparatus of claim 23, wherein the combination of said first adsorbents is either in the form of a mixture of adsorbents or a composite adsorbent.
- [0035] 35. The apparatus of claim 23, wherein said first adsorbents are clinoptilolite and chabazite, and wherein said clinoptilolite and chabazite are either natural or synthetic and have exchangeable cations selected from the group consisting of cations of Group 1A, Group 2A, Group 3A, Group 3B, the lanthanide series and combinations thereof.

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[0036] 36. The apparatus of claim 23, wherein said apparatus is an air prepurifier.

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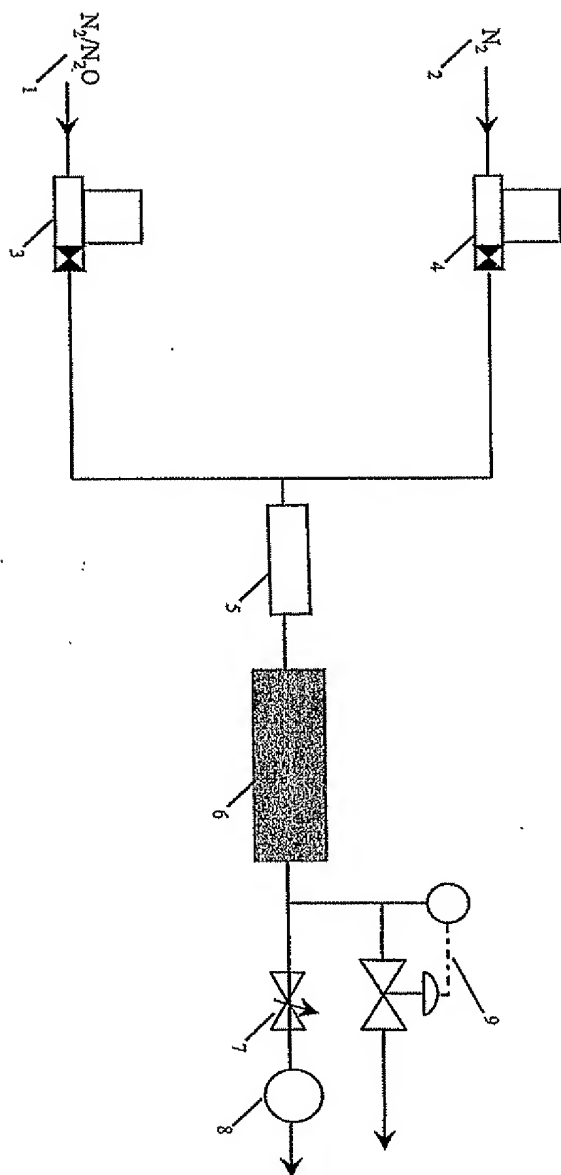


Figure 1

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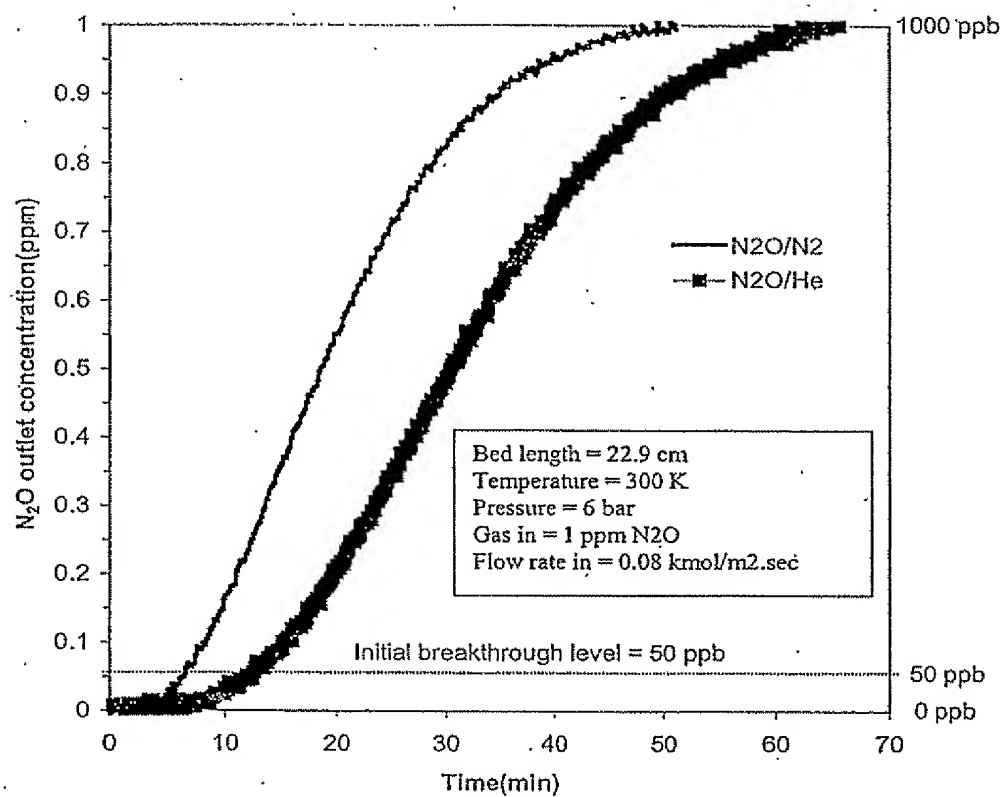


Figure 2

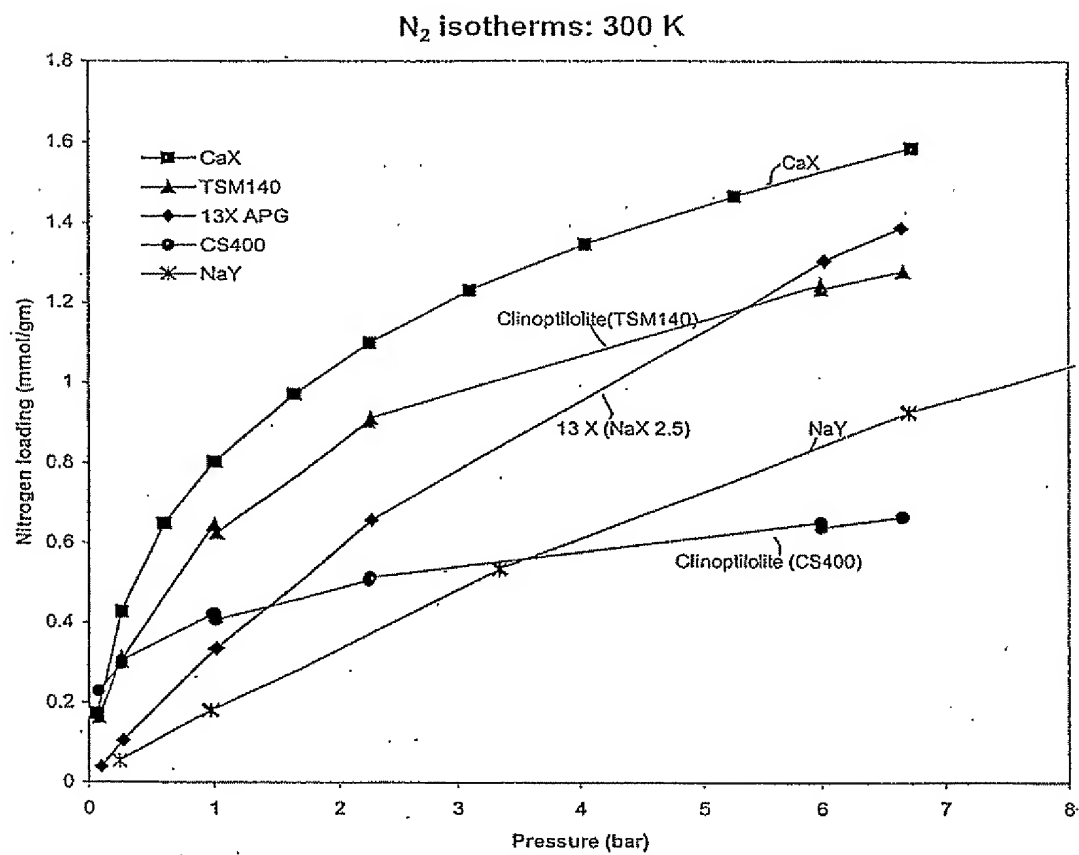


Figure 3.

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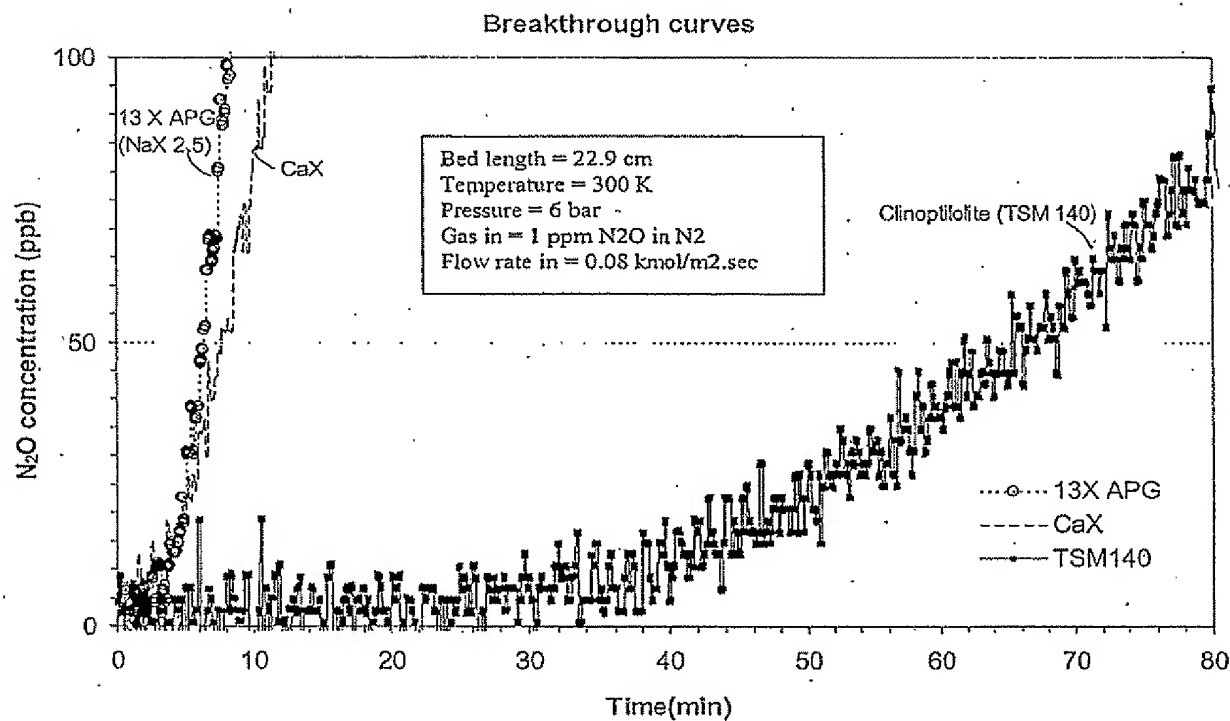


Figure 4

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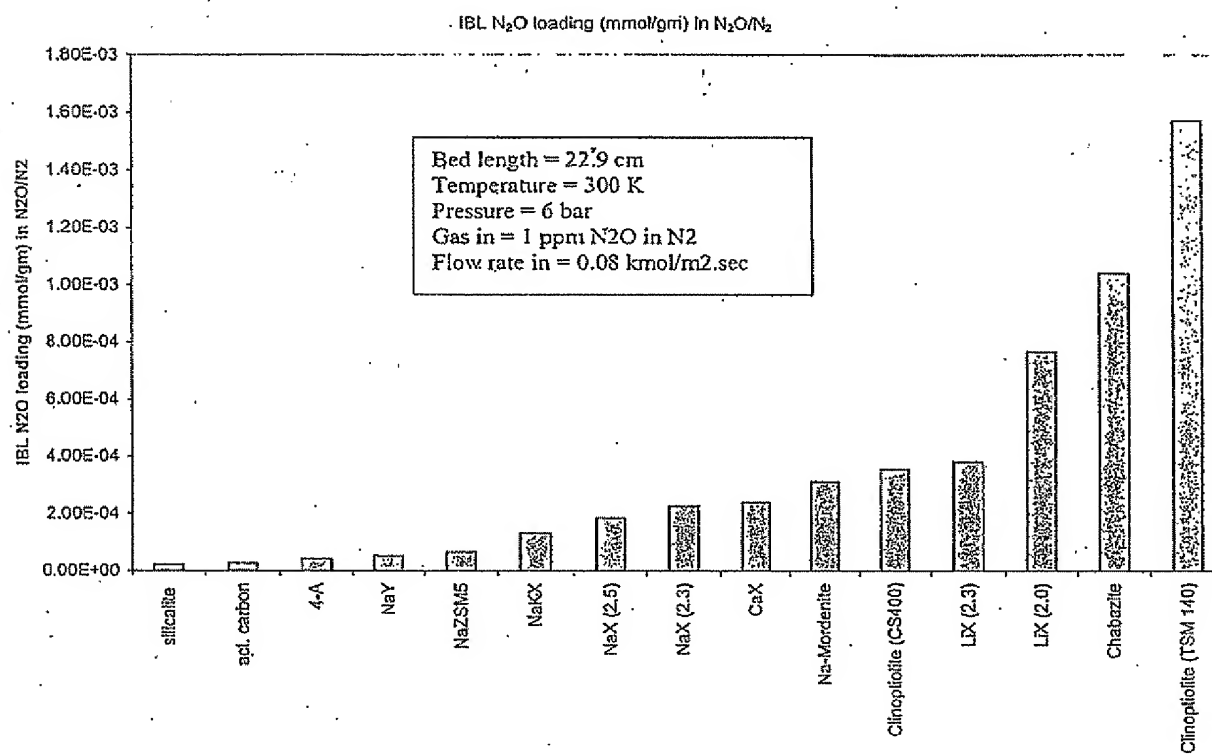


Figure 5.

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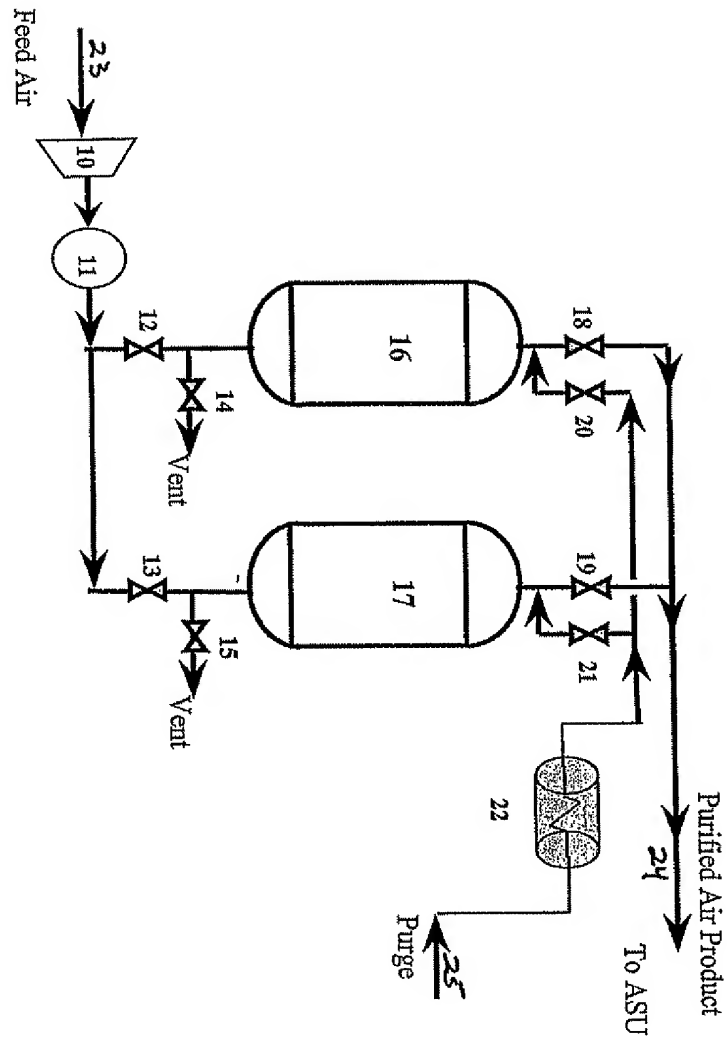


Figure 6.

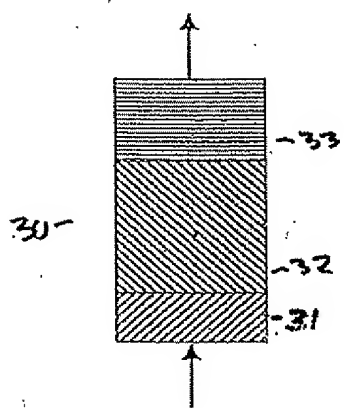


Fig. 7a

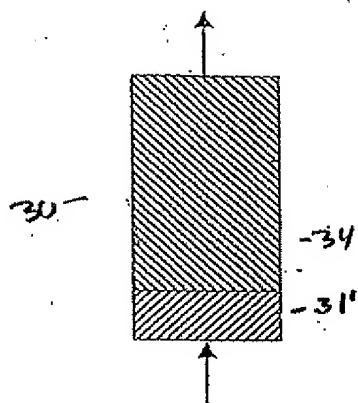


Fig. 7b

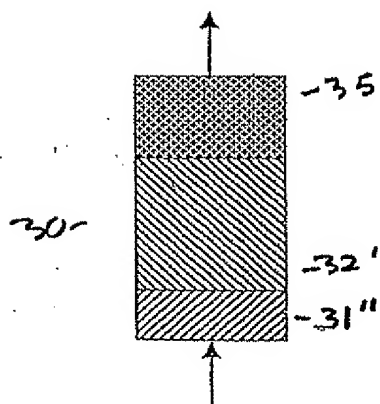


Fig. 7c

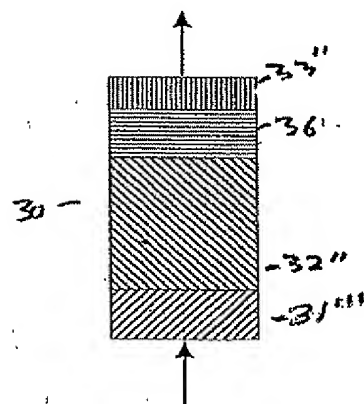


Fig. 7d

Figure 7

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/40591

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : B01D 53/047

US CL : 95/96,106,119,123,129,139,902; 96/130,132

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 95/96-106,117-120,123,129,139,902; 96/130-133,143,144

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,507,271 A (VAN DEYCK et al.) 26 March 1985 (26.03.85).	1-36
A	US 4,933,158 A (ARITSUKA et al.) 12 June 1990 (12.06.90).	1-36
A	US 4,935,580 A (CHAO et al.) 19 June 1990 (19.06.90).	1-36
A	US 4,964,889 A (CHAO) 23 October 1990 (23.10.90).	1-36
A	US 5,587,003 A (BULOW et al.) 24 December 1996 (24.12.96).	1-36
A	US 5,919,286 A (GOLDEN et al.) 06 July 1999 (06.07.99).	1-36
A	US 5,938,819 A (SEERY) 17 August 1999 (17.08.99).	1-36
A	US 6,106,593 A (GOLDEN et al.) 22 August 2000 (22.08.00).	1-36
A,P	US 6,358,302 B1 (DENG et al.) 19 March 2002 (19.03.02).	1-36



Further documents are listed in the continuation of Box C.



See patent family annex.

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"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

01 April 2003 (01.04.2003)

Date of mailing of the international search report

01 MAY 2003

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INTERNATIONAL SEARCH REPORT

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C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A,P	US 6,391,092 B1 (SHEN et al.) 21 May 2002 (21.05.02).	1-36